Differential scanning calorimetry of minerals of the dolomite-ferroan-dolomite-ankerite series in flowing carbon dioxide

J. V. DUBRAWSKI

BHP Central Research Laboratories, PO Box 188, Wallsend, NSW 2287, Australia

AND

S. ST. J. WARNE

Department of Geology, University of Newcastle, Shortland, NSW 2308, Australia

Abstract

The dolomite-ferroan-dolomite-ankerite series of carbonate minerals has been investigated in flowing carbon dioxide using high-temperature DSC. Decomposition products were analysed by X-ray diffraction. The minerals studied included dolomite containing no iron, and members substituted by iron in the molar ratio range of 0.082 to 0.49. Complete resolution of the three main endothermic features was observed and enthalpy values ΔH, determined from each. The individual and total enthalpy values showed a linear dependence upon the Fe and Mg content of the members across the series. A decrease in the enthalpy of decomposition occurs with increasing Fe content. The effect of Fe substitution was readily observed and the estimated limit of detection is less than 1% FeO. Accuracy of the measurements was limited by the purity of the minerals themselves.

KEYWORDS: dolomite, ferroan dolomite, ankerite, differential scanning calorimetry, X-ray diffraction, carbon dioxide.

Introduction

THE dolomite-ferroan-dolomite-ankerite mineral series represents an important group of carbonates that have been studied by the well-established techniques of differential thermal analysis (DTA) and thermogravimetry (TG). The DTA curve for dolomite, the first member of the series, is well known and reveals two endothermic peaks in the presence of CO_2 at product gas concentration. The lower-temperature peak is believed to be associated with breakdown of the dolomite structure/magnesium carbonate component and the higher-temperature peak with remaining calcium carbonate. The mechanism of decomposition has been investigated extensively (Haul *et al.*, 1951; Kulp *et al.*, 1951; Haul and Heystek, 1952; Haul and Wilsdorf, 1952; Bandi and Krapf, 1976) and the subject has been reviewed by Otsuka (1986).

The dolomite-ankerite group consists of a solid solution between the theoretical limits $CaMg(CO_3)_2$–$CaFe(CO_3)_2$ and contains increasing replacement of Mg^{2+} by Fe^{2+} up to a mole fraction limit of approximately 0.7 $CaFe(CO_3)_2$. Many ferroan dolomites have also been studied using DTA (Beck, 1950; Kulp *et al.*, 1951; Stadler, 1964; Smykatz-Kloss, 1964; Todor, 1976; Iwafuchi *et al.*, 1983; Otsuka, 1986). Essentially three endotherms, each accompanied by a weight loss, and an exotherm succeeding the first endotherm were reported in air.

Resolution of the endothermic peaks is complete in flowing carbon dioxide (Warne *et al.*, 1981) and confirms in detail the earlier reports that increasing Fe decreases the peak temperature of the first endotherm, and the peak area of the second endotherm increases. The various DTA curves reported however have been interpreted differently (Beck, 1950; Stadler, 1964; Smykatz-Kloss, 1964; Todor, 1976; Iwafuchi *et al.*, 1983; Otsuka, 1986)

Table 1 Chemical Analysis of Dolomite-Ankerite Mineral Series

Sample[+]	% CaO	% FeO	% MnO	% MgO	% CO_2	Total
1 Dolomite	30.78	–	0.06	20.88	46.99	98.71
$Ca_{1.028}Mn_{0.0016}Mg_{0.970}(CO_3)_2$						
2 Ferroan Dolomite	29.00	3.10	0.46	19.80	46.56	98.92
$Ca_{0.978}Fe_{0.0816}Mn_{0.012}Mg_{0.929}(CO_3)_2$						
3 Ferroan Dolomite	30.87	5.43	1.32	16.16	46.02	99.80
$Ca_{1.053}Fe_{0.145}Mn_{0.036}Mg_{0.767}(CO_3)_2$						
4 Ferroan Dolomite	29.43	8.37	2.15	14.52	45.41	99.88
$Ca_{1.017}Fe_{0.226}Mn_{0.059}Mg_{0.698}(CO_3)_2$						
5 Ankerite	28.83	15.02	1.09	10.70	44.18	99.82
$Ca_{1.024}Fe_{0.417}Mn_{0.031}Mg_{0.529}(CO_3)_2$						
6 Ankerite	28.13	15.11	1.12	11.21	44.28	99.85
$Ca_{0.997}Fe_{0.418}Mn_{0.032}Mg_{0.553}(CO_3)_2$						
7 Ankerite	28.93	17.51	0.67	9.11	43.78	100.0
$Ca_{1.037}Fe_{0.490}Mn_{0.019}Mg_{0.454}(CO_3)_2$						

[+] Carbonate minerals 1 to 7 are from: 1 British chemical standard

dolomite (BCS 368); 2 Kalgoorlie, W. Australia; 3 Wallaroo,

S. Australia; 4 Tintagel, England; 5 Teruel, Spain; 6 Gollrad

Mürzsteg, Styria; and 7 Blue Rock Tunnel, Pa, USA.

Studies involving TG–DTA–EGA curves for ankerite in flowing CO_2 have been carried out by Milodowski and Morgan (1981).

The heats of decomposition of carbonate minerals, including dolomite and ankerite, have been determined (Reddick, 1968) by DTA in a dynamic CO_2 atmosphere. Differential scanning calorimetry (DSC) has not been used to any great extent in mineralogical carbonate studies to date although its applicability has been demonstrated (Dubrawski and Warne, 1987). Recently members of the dolomite–ankerite series have been investigated using this technique and X-ray diffraction (Warne and Dubrawski, 1987). The enthalpy of decomposition for each member of the series was measured in flowing nitrogen and found to decrease linearly with increasing Fe content. The present paper describes the study of this series in flowing carbon dioxide where complete resolution of peaks was expected to occur. In particular,

the enthalpy of the second endotherm, which is dependent on iron substitution, could be measured independently of the total enthalpy.

Experimental

All DSC curves were recorded on a Rigaku Denki Thermoflex 8100 series instrument consisting of TG, DTA and DSC modular units. The sensitivity of the DSC unit ranged from ± 0.5 to 16 mcal/sec and was operative to about 950 °C. Samples were heated in platinum cups covered with polished platinum lids. Calcined alumina was used as the thermal reference material. Experiments were carried out in high-purity flowing carbon dioxide (200 ml/min).

Calibration of the instrument was done using a series of simple salts (International Confederation of Thermal Analysis, ICTA, Standards) as described earlier (Breuer and Eysel, 1982; Dubrawski

and Warne, 1986). Consequently the 'instrument parameter' K was determined over the temperature ranges of 400–900 °C.

The minerals studied belong to the dolomite–ferroan-dolomite–ankerite series, for which chemical analyses were obtained as shown in Table 1. All samples were reduced to $< 50~\mu$m particle size prior to thermal analysis. Sample masses

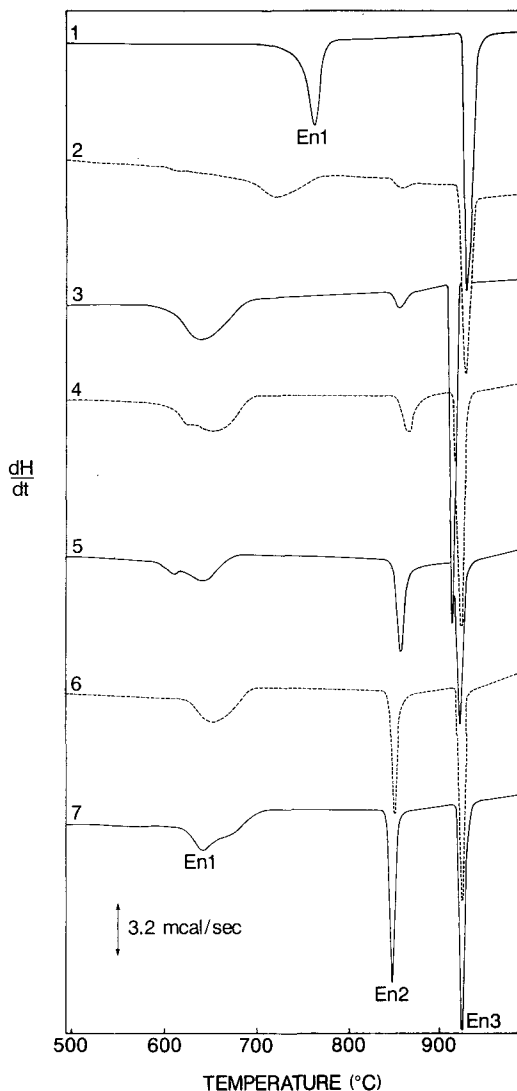FIG. 1. DSC curves of the dolomite–ankerite mineral series in flowing carbon dioxide. 1, dolomite (8.02 mg); 2, ferroan dolomite 2 (7.27 mg); 3, ferroan dolomite 3 (7.36 mg); 4, ferroan dolomite 4 (8.66 mg); 5, ankerite 5 (7.14 mg); 6, ankerite 6 (7.73 mg); 7, ankerite 7 (8.63 mg). For clarity alternate curves are shown as full and dashed lines.
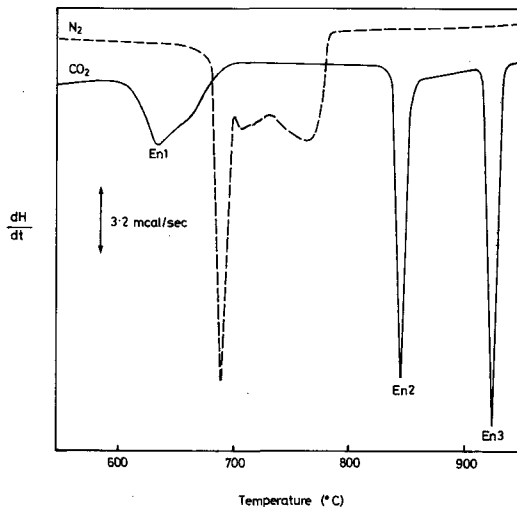

FIG. 2. DSC curves of $Ca_{0.997}Fe_{0.418}Mn_{0.032}Mg_{0.553}$ $(CO_3)_2$ in flowing CO_2 and N_2.

throughout were in the range 5–50 mg and the heating rate 10 °C/min. Chart speed was maintained within the range 5–20 mm/min. Peak areas were measured using a Tamaya Planix 7 planimeter, and base-lines were drawn according to the criteria established by O'Neill (1966), Guttman and Flynn (1973).

Calculated heats of reaction for dolomite and dicalcium ferrite were obtained from data stored in the CSIRO-SGTE Thermodata system. Measured enthalpies were obtained from the equation

$$\Delta H . M = K . A \qquad (1)$$

where ΔH is the energy (mJ/mg) for a given thermal process, M the sample mass (mg), K the 'instrument parameter' and A the peak area normalised to energy values.

Decomposition products were analysed by X-ray diffraction (XRD) using a Siemens D-500 diffractometer and Cu-$K\alpha$ radiation. A graphite monochromator was employed to eliminate $K\beta$ radiation and fluorescence.

Results and Discussion

DSC determinations in flowing carbon dioxide. The DSC curves resulting from heating minerals of the dolomite–ankerite series in flowing carbon dioxide are shown in Fig. 1. Three distinct sets of peaks are obtained for each member with the exception of dolomite which only yields two. The effect of CO_2 upon peak resolution is easily appreciated by comparison of DSC curves for the

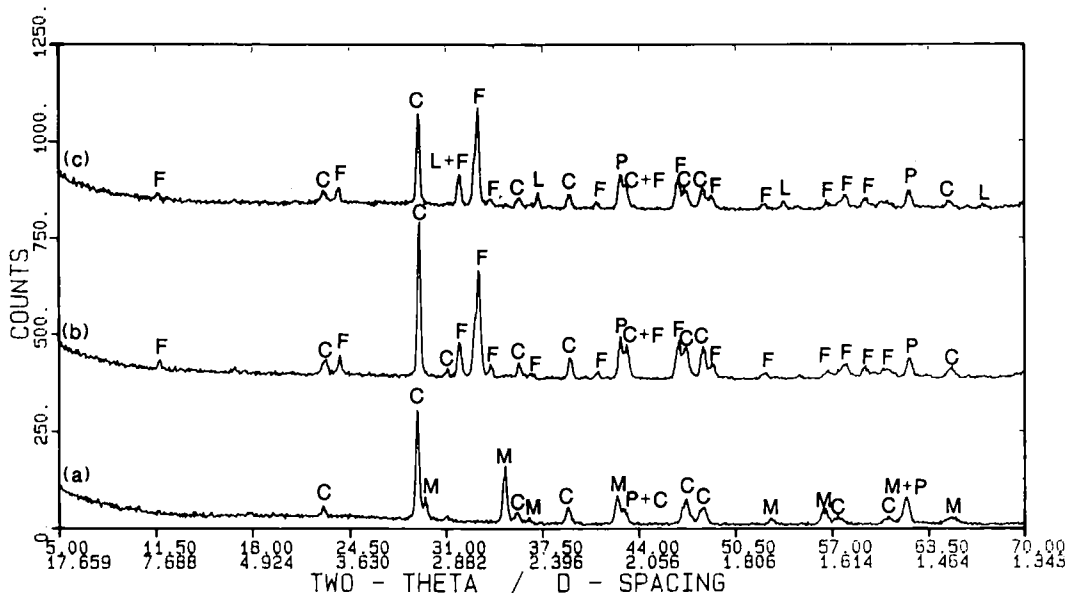FIG. 3. XRD patterns of decomposition products from heating $Ca_{1.024}Fe_{0.417}Mn_{0.031}Mg_{0.529}(CO_3)_2$ in CO_2 to (a) 750 °C (b) 900 °C and (c) 1000 °C. Phases observed: C, $CaCO_3$; M, $MgO . Fe_2O_3/FeO . Fe_2O_3$; P, MgO; F, $2CaO .$ Fe_2O_3; L, CaO.

ankerite $Ca_{1.037}Fe_{0.490}Mn_{0.019}Mg_{0.454}(CO_3)_2$, obtained in N_2 and CO_2 and shown in Fig. 2. It is apparent that in flowing CO_2, compared to N_2, the first endotherm of the curve moves to a lower temperature and broadens into a peak and shoulder (En 1), while the second and third broader endotherms move to higher temperatures and become attenuated (En 2-3). This is the trend followed by all members of the series in CO_2. In CO_2, the temperature spread between first and last peaks is 340 °C, while in N_2 it is 110 °C, representing a factor of three in enhanced thermal resolution.

Returning to Fig. 1, the three endothermic peaks for each mineral have been designated En1, En2 and En3 respectively. It is noteworthy that in CO_2 En1 is broadened, sometimes appears composed of two peaks, or attended by a high-temperature shoulder in several instances, while En2 and En3 are single and fairly sharp endotherms.

The first endotherm En1 shifts to lower temperatures along the series, except for the last two high-Fe content members (Fig. 1, curves 6 and 7). Both the peak shape and temperature shifts differ from earlier work (Warne et al., 1981) in CO_2, where only a single peak was observed and a consistent temperature drop across the series occurs. It would appear that the improved resolution with DSC indicates En1 to be the result of a composite

reaction, partially resolved, whereas in DTA only a single averaged thermal event is detected. This confirms the DTG results of Milodowski and Morgan (1981).

The peak temperatures observed for the series are shown in Table 2. En1 shifts from 763 to 643 °C, En2 appears with iron substitution and occurs in the range 850-860 °C. The high-temperature peak En3 is also fairly static and with one exception occurs between 925-935 °C.

X-ray diffraction analysis of dolomite-ankerite decomposition products. Following the DSC curves from Fig. 1 samples of the mineral specimens were heated in flowing CO_2 to temperatures just beyond the completion of each thermal reaction En1, En2 and En3. The individual products were collected for X-ray analysis. As an example, Fig. 3 shows the diffraction patterns obtained from the decomposition products of $Ca_{1.024}Fe_{0.417}Mn_{0.031}$ $Mg_{0.529}(CO_3)_2$. Pattern (a) corresponds to the products obtained at the end of En1 (approx. 750 °C), (b) to those after En2 (approx. 900 °C) and (c) to products from the completion of En3 (1000 °C).

With the exception of dolomite, which yields only CaO and MgO as its products, the remaining ferroan-dolomite-ankerite minerals undergo a complex series of reactions. Earlier work (Kulp et al., 1951, and Smith, 1972) has suggested that

Table 2   Peak Temperatures ($^\circ$C), and Calculated Enthalpies (ΔH) for Minerals of the Dolomite-Ankerite Series*

Mineral	En1	En2	En3	ΔH_1	ΔH_2	ΔH_3	ΔH_R
		($^\circ$C)			(kJ mol^{-1})		
1. Dolomite	763	–	935	97±4	0.0	192±4	289±8
2. Ferroan dolomite	720	857	933	110±5	4.5±1	168±3	283±9
3. Ferroan dolomite	633	855	916	91±2	13±1	166±6	270±9
4. Ferroan dolomite	628,658	862	923	79±2	29±3	152±3	260±8
5. Ankerite	609,641	855	922	58±3	71±3	104±4	233±10
6. Ankerite	656	850	927	61±3	65±3	112±3	238±9
7. Ankerite	643	850	929	49±3	75±2	101±3	226±8

*Instrument parameter values (K): K_1 determined to be in the range 1.34-1.18 for ΔH_1; K_2 = 1.46 for ΔH_2: K_2 = 1.56 for ΔH_3.

the first reaction of these carbonates results in decomposition of both $FeCO_3$ and $MgCO_3$ followed by oxidation of FeO to yield, in CO_2, $CaCO_3$, MgO and $MgO \cdot Fe_2O_3$. Milodowski and Morgan (1981) reported that Fe_2O_3 forms from the oxidation of FeO, and subsequently reacts with MgO to form magnesioferrite ($MgO \cdot Fe_2O_3$). Magnetite is also formed. Based on these reports En1 is believed to consist of the following reaction steps (Earnest, 1984).

$$Ca(Mg_{1-x},Fe_x)(CO_3)_2 \rightarrow CaCO_3 + xFeO +$$
$$(1-x-y)MgO + yMgCO_3 + (1-y)CO_2 \quad (2)$$

$$2FeO + CO_2 \rightarrow Fe_2O_3 + CO \quad (3)$$

$$MgO + Fe_2O_3 \rightarrow MgO \cdot Fe_2O_3 \quad (4)$$

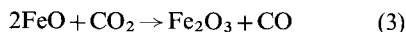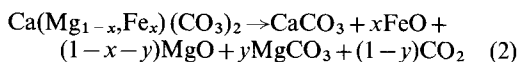$$FeO + Fe_2O_3 \rightarrow FeO \cdot Fe_2O_3 \quad (5)$$

Fig. 3(a) reveals the products of En1 to be calcium carbonate, magnesium oxide and magnetite ($FeO \cdot Fe_2O_3$). Peaks due to magnesioferrite and magnetite overlapped since their diffraction patterns are quite similar ($MgO \cdot Fe_2O_3$, major peak 2.53 A; $FeO \cdot Fe_2O_3$, major peak 2.52 A). The observed products from the dolomite–ankerite specimens agreed with the scheme proposed above. Residual undecomposed $MgCO_3$ as indicated in equation (2) is believed to exist in solid solution with $CaCO_3$ and is gradually eliminated at higher temperature (Earnest, 1984).

The products of En2 are shown in Fig. 3(b). New peaks were due to the formation of non-magnetic dicalcium ferrite ($2CaO \cdot Fe_2O_3$). Slight shifts in peak position suggested that some substitution by magnesium still remained. The appearance of this ferrite phase supports the claim (Milodowski and Morgan, 1981) that En2 results from the reaction,

$$2CaCO_3 + MgO \cdot Fe_2O_3 \rightarrow$$
$$2CaO \cdot Fe_2O_3 + MgO + 2CO_2 \quad (6)$$
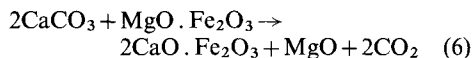
Finally, En3 results from the breakdown of any remaining calcium carbonate to CaO. Thus,

$$CaCO_3 \rightarrow CaO + CO_2 \quad (7)$$
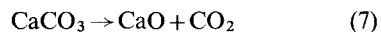
The presence of CaO, however, was absent in some cases, since the decomposition products, on cooling in CO_2, recarbonated to $CaCO_3$. This explains the prominent carbonate peaks that appear in Fig. 3(c).

Determinations of ΔH and its relationship to substitution. The peak resolution afforded by flowing CO_2 allowed the application of equation (1) to each peak En1, En2 and En3, for which an individual ΔH value was determined. From a calibration plot of the instrument parameter against temperature as described earlier (Dubrawski and Warne, 1986), a K value was obtained for each peak temperature. The values used are shown in Table 2, designated K_1, K_2 and K_3, corresponding with each endotherm. Enthalpy values determined from the endotherms were designated ΔH_1, ΔH_2 and ΔH_3 respectively and are shown in Table 2. They are the enthalpies corresponding with each of the three decomposition stages indicated in the
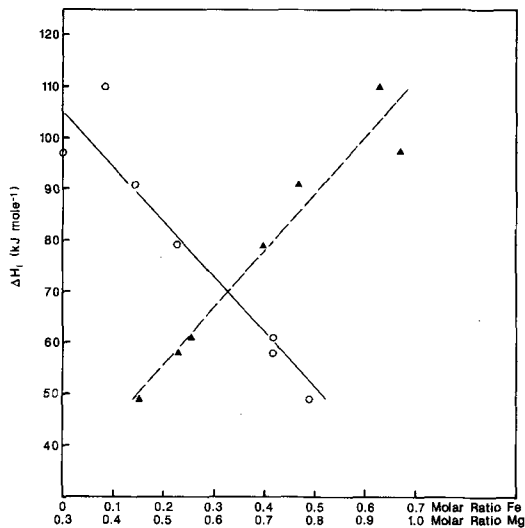
FIG. 4. Plot of enthalpy ΔH_1 versus mole fraction substituted iron (o) and magnesium (▲).

last section. The DSC curves for each mineral in the series were obtained from numerous runs (6–10) using sample masses in the range 5–25 mg. Enthalpy values were calculated from the peak areas of each curve and averaged. Earlier it was shown (Dubrawski and Warne, 1986) that for a range of minerals, heated over a wide temperature span, the precision in the measurement of enthalpy is about 5% relative.

The individual enthalpy values from each peak were found to be dependent upon substituted iron content. Conversely, a dependence upon magnesium also appeared since it decreased with increasing Fe content.

Fig. 4 shows a plot of ΔH_1 against molar ratio Fe and Mg. The value of ΔH_1 for dolomite is about 100 kJ mol^{-1}, close to the figure for magnesite (110 kJ mol^{-1}) and indicates that En1 is linked thermally to breakdown of the $MgCO_3$ component of the mineral. With the ferroan dolomite-ankerites En1 is broadened or split due to the presence of several thermal processes, as outlined earlier. A general decrease in ΔH_1 with increasing iron content is observed (increasing with Mg), although ΔH_1 for ferroan dolomite (No. 2) containing 0.0816 Fe content, is unexpectedly high. While En1 endotherms (Fig. 1) indicate a complex thermal process, they also differ from earlier reported DTA curves (Warne et al., 1981) which revealed a single relatively sharp endotherm.

Fig. 5 shows the relationship of ΔH_2 with Fe and Mg content. It quantitatively establishes the linear relationship between Fe content and the

endotherm En2 first noted qualitatively using DTA (Warne et al., 1981). As mentioned earlier En2 results in the formation of dicalcium ferrite (equation 6). The standard enthalpy for this reaction was calculated to be about 330 kJ/mole, on a molar basis of magnesioferrite ($MgO . Fe_2O_3$). Because of the various reactions occurring in process En1 it is difficult to establish the actual consumption of iron and magnesium from the parent carbonate during formation of the calcium ferrite. Nevertheless, let us assume that all FeO from the carbonate reacts to form Fe_2O_3 and subsequently $MgO . Fe_2O_3$. This means that, say 0.5 moles FeO yield 0.25 moles $MgO . Fe_2O_3$ (Mg is always in excess), then, using the molar ratios of Fe in the ankerites containing the highest Fe levels (namely samples 5, 6 and 7) and their corresponding ΔH_2 values, one can calculate the ΔH_2 per mole of Fe_2O_3 (and, therefore, $MgO . Fe_2O_3$). Such calculations yield values between 300 and 340 kJ/mole for the three ankerites mentioned. While these figures are approximate and remembering the assumptions above, nevertheless the measured ΔH_2 yields figures that are consistent with the formation of $2CaO . Fe_2O_3$ in process En2. It can also be said in relation to En2 that DSC is sensitive even to low levels of iron substitution. In Fig. 1, ferroan dolomite sample 2, containing 3 wt. % FeO, produces a readily discernible peak even at the least sensitive instrument setting. Since a tenfold enhancement of instrumental sensitivity is available, substitution of Mg in dolomite by iron in amounts below 1 wt. % should be detectable.
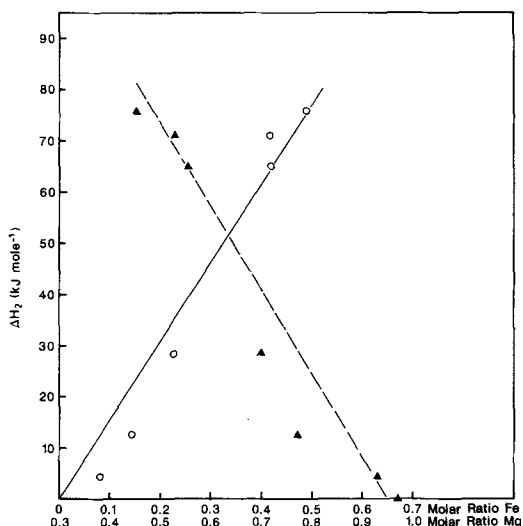

FIG. 5. Plot of enthalpy ΔH_2 versus mole fraction substituted iron (o) and magnesium (▲).

Table 3 Molar Ratio of Iron and Manganese in the Dolomite-Ankerite Series and Enthalpy (ΔH_2) of the Second Endotherm

Sample	Molar Ratio Fe	Molar Ratio Mn	$\frac{Fe}{Mn}$	ΔH_2 (kJ mol^{-1})
1 Dolomite	0.0	0.0016	0.0	0.0
2 Ferroan dolomite	0.0816	0.012	6.8	4.5
3 Ferroan dolomite	0.145	0.036	4.0	13
4 Ferroan dolomite	0.226	0.059	3.8	29
5 Ankerite	0.417	0.031	13.5	71
6 Ankerite	0.418	0.032	13.1	65
7 Ankerite	0.490	0.019	25.8	75

It is apparent, however, that the early members of the series (Fe content 0.08-0.2) yield ΔH_2 values generally lower than expected for a good linear fit. A possible cause is the significant levels of Mn substitution relative to Fe that occurs in these samples. Table 3 shows the Fe and Mn content, and the ratio of the former to the latter. The ratio is smaller for the early members, about 4-6, as opposed to 15-25 for the later members of the series. The early members, therefore, react thermally as ferromanganoan dolomites, which causes the determined enthalpies to reflect the value of this series. The decomposition of ferromanganoan dolomites has been investigated by Iwafuchi *et al.* (1983) who has reported the formation of $CaMnO_3$ and $(Fe,Mn)_3O_4$ in addition to the other expected products.

The En3 peak results from the decomposition of unreacted $CaCO_3$ and a plot of ΔH_3 against Fe and Mg content also yields straight lines (Fig. 6). For dolomite, where the Fe content is zero, ΔH_3 is about 190 kJ mol^{-1}, about 10% higher than the value for calcite. The value of ΔH_3 decreases with increasing Fe since less $CaCO_3$ is present per mole of mineral due to increased reaction with magnesioferrite in the process that produces En2. In fact ΔH_3 is essentially halved in going from 0 to 0.5 mole fraction Fe substitution.

The enthalpy of decomposition ΔH_R

The sum of the measured enthalpies ΔH_1, ΔH_2 and ΔH_3 for any member of the series yields ΔH_R, the total enthalpy of decomposition for that member. From Table 2 ΔH_R for dolomite is calculated to be 289 kJ mol^{-1} which is in good agreement with the value determined earlier in flowing nitrogen (Dubrawski and Warne, 1987;
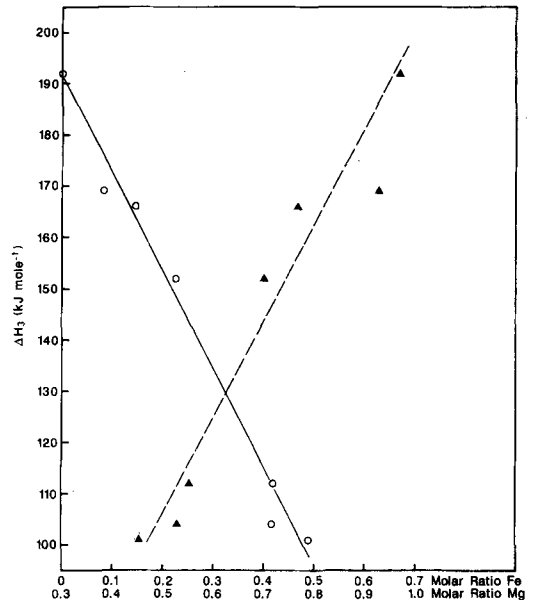

FIG. 6. Plot of enthalpy ΔH_3 versus mole fraction substituted iron (o) and magnesium (▲).

Warne and Dubrawski, 1987). The literature (Robie *et al.*, 1979) gives a value of about 280 kJ mol^{-1}. The ΔH_R values decrease with Fe substitution or conversely, increase with increasing Mg substitution, and a straight line is obtained (Fig. 7). Due to a solubility barrier, the end member of the series occurs naturally at 0.7 mole fraction $CaFe(CO_3)_2$. From Fig. 7 it can be estimated that the ΔH_R value of this end member would be about 200 kJ mol^{-1}.

The results presented provided no mechanistic

details but are consistent with the proposals of Milodowski and Morgan (1981) and Iwafuchi *et al.* (1983). Due to the nature of the sequential reactions that take place in the breakdown of the dolomite–ankerites, the enthalpy values are necessarily linked. Thus, ΔH_1 and ΔH_3 mutually decrease as ΔH_2 rises, but the ratio $\Delta H_3/\Delta H_1$ remains close to the value 2 throughout the series (the exception is ferroan dolomite sample 2). The magnesium oxide formed during En1 and increasingly consumed by substituted iron (to form magnesioferrite) is matched proportionately by the calcium carbonate consumed by magnesioferrite in the process associated with En2, and a stable ratio of values is obtained.
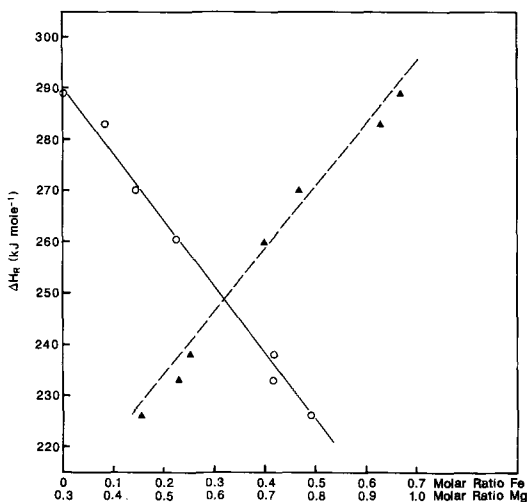

FIG. 7. Plot of total enthalpy ΔH_R versus mole fraction substituted iron (o) and magnesium (▲).

It is clear that ΔH_R or the other enthalpies, particularly ΔH_2, can be used to distinguish members of the series and establish the degree of iron substitution. From Table 2, however, it is apparent that ΔH_R and ΔH_2 are reliable to within about 4% and 5–20% relative, respectively, which therefore limits the extent to which close members can be distinguished. The accuracy of these values is dependent upon the purity (e.g. Mn substitution) of mineral specimens. No reliable enthalpy data, however, are available to assist in any comparison. Nevertheless, the results clearly show that DSC is quite sensitive to even low levels of substitution and to the effects of substitution (by Fe or Mn) and that the trend of measured enthalpies is systematic and useful to an understanding of these reactions.

Conclusions

(1) DSC can be used to measure enthalpies of mineral phases that otherwise are not available nor readily established theoretically. Thus, the iron-substituted end member of the dolomite–ankerite series is estimated to possess a ΔH_R value of approximately 200 kJ mol^{-1}.

(2) The relationship between the determined enthalpy values and substituted iron content was found to be linear.

(3) The effect of iron substitution was readily apparent from the DSC curves of the ferroan-dolomite–ankerite minerals. The detection limit for iron substitution is estimated to be below 1 wt. % FeO.

(4) The accuracy of DSC measurements is limited by the purity of the minerals themselves. Determinations of ΔH_1 and ΔH_2 were occasionally variable, an effect attributed to variable amounts of substituted Mn.

(5) The DSC curves and calculated enthalpies are consistent with the proposed mechanism (Milodowski and Morgan, 1981) for the decomposition of dolomite–ankerite minerals. Qualitatively some differences occur between the DSC curves and earlier reported DTA curves.

Acknowledgements

References

Bandi, W. R. and Krapf, G. (1976) The effect of CO_2 pressure and alkali salt on the mechanisms of decomposition of dolomite. *Thermochim. Acta*, **14**, 221–43.

Beck, C. W. (1950) Differential thermal analysis curves of carbonate minerals. *Am. Mineral.* **35**, 985.

Breuer, K. H. and Eysel, W. (1982) The calorimetric calibration of differential scanning calorimetry cells. *Thermochim. Acta*, **57**, 317–29.

Dubrawski, J. V. and Warne, S. St. J. (1986) Calibration of differential scanning calorimetry units for mineralogical studies. Ibid. **104**, 77–83.

——(1987) The use of differential scanning calorimetry in measuring the thermal decomposition of mineral carbonates occurring in coal. *Fuel*, **66**, 1733–6.

Earnest, C. M. (1984) *Thermal analysis of clays, minerals and coal.* Perkin-Elmer Corp., Norwalk, USA, 16 pp.

Guttman, C. M. and Flynn, J. H. (1973) On the drawing of the base line for differential scanning calorimetric calculation of heats of transition. *Anal. Chem.* **45**, 408–10.

Haul, R. A. W. and Heystek, H. (1952) Differential thermal analysis of the dolomite decomposition. *Am. Mineral.* **37**, 166–79.

—— and Wilsdorf, H. (1952) Rontgenographische untersuchung der thermischen zersetzung von dolomitkristallen. *Acta Crystallogr.* **5,** 250–5.

—— Stein, L. H., and Louw, J. D. (1951) Exchange of carbon-13 dioxide between solid carbonates and gaseous carbon dioxide. *Nature* (London) **167,** 241.

Iwafuchi, K., Watanabe, C., and Otsuka, R. (1983) Thermal decomposition of ferromanganoan dolomite. *Thermochim. Acta,* **66,** 105–25.

Kulp, J. L., Kent, P., and Kerr, P. F. (1951) Thermal study of the Ca–Mg–Fe carbonate minerals. *Am. Mineral.* **36,** 643–70.

Milodowski, A. E. and Morgan, D. J. (1981) *Thermal decomposition of minerals of the dolomite-ferroan dolomite-ankerite series in a carbon dioxide atmosphere.* Proc. 2nd ESTA Conference. Aberdeen, Scotland, pp. 468–71.

O'Neill, M. J. (1966) Measurement of specific heat functions by differential scanning calorimetry. *Anal. Chem.* **38,** 10, 1331–6.

Otsuka, R. (1986) Recent studies in the decomposition of the dolomite group by thermal analysis. *Thermochim. Acta,* **100,** 69–80.

Reddick, K. L. (1968) *Heats of reaction for carbonate mineral decomposition.* Anal. Calorimetry, Proc. Amer. Chem. Soc. Symp., 155th, 297–303. Edited by Porter, R. S., Plenum Press, New York.

Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1979) *Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar pressure and at higher temperatures.* Geological Survey Bulletin 1452 US Government Printing Office, Washington.

Smith, J. W. (1972) *Thermal analysis in earth science: experience and expectations.* Thermal Analysis V. III (Proc. 3rd ICTA) Birkhauser Verlag, Basel, 605–35.

Smykatz-Kloss, W. (1964) Differential thermo-analyse von einigen karbonat-mineralen. *Beitr. Mineral. Petrogr.,* **9,** 481–502.

Stadler, H. A. (1964) Petrographische und mineralogische untersuchungen im Grimselgebiet. *Schweiz. Mineral. Petrogr. Mitt.,* **44,** 187–399.

Todor, D. N. (1976) *The thermal analysis of minerals.* Abacus Press, Tunbridge Wells, UK, 256 pp.

Warne, S. St. J. and Dubrawski, J. V. (1987) Differential scanning calorimetry of the dolomite-ankerite mineral series in flowing nitrogen. *Thermochim. Acta,* **121,** 39.

—— Morgan, D. J., and Milodowski, A. E. (1981) Thermal analysis studies of the dolomite, ferroan dolomite, ankerite series. Part 1. Iron content recognition and determination by variable atmosphere DTA. *Ibid.* **51,** 105–11.